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Phase transformations occurring in Ni-rich NiAl during quenching

R. MOSKOVIC
Department of Metallurgy and Materials Science, University of Cambridge, Pembroke Street, Cambridge, UK

Quenching of Ni-rich NiAl is accompanied by the formation of fine planar precipitates on {110} matrix planes and martensite is produced. Martensite is shown to have a body centred tetragonal crystal structure which can form from the high temperature NiAl B2 crystal structure by a process involving an inverse Bain correspondence. Since further ordering of martensite occurs during quenching a superordered martensite crystal structure is proposed. This structure is characterized by alternate stacking of Ni atoms and Ni or Al atoms on (0 1 1) planes. The martensite plates are internally twinned in $\{1\,0\,1\}_T$ $[1\,0\,1]_T$.

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1. Introduction

Quenching of Ni-rich NiAl solid solutions, from temperatures above 1000° C, is known to produce martensite, the crystal structure of which was determined by Rosen & Goebl [1]. These workers used a combination of powder X-ray diffraction and diffractometer traces to study the structure of the Ni–34 at.% Al alloy quenched from 1300° C and annealed at 600° C. They proposed a modified CuAu-type crystal structure (face centred tetragonal, f c tet) with a c/a ratio of 0.86. This crystal structure cannot be formed directly from a B2-type NiAl crystal structure by local atomic interchange. To facilitate the formation of martensite, an ordered Ni-rich NiAl structure, existing above the M_s temperature, was postulated. However, X-ray diffraction measurements at 800 to 1000° C did not confirm its presence. The crystal structure of NiAl martensite, which was proposed by Rosen and Goebl, is inconsistent with the transmission electron microscopy results of Enami *et al.* [2]. The latter workers proposed that the NiAl martensite has an LI_0 crystal structure (CuAu I type) and suggested that the most likely mode of formation of the martensite was by an inverse Bain correspondence. Enami *et al.* [2] also found that the martensite was internally twinned in $\{1\,1\,1\}_T$ $\langle 1\,1\,2\rangle_T$.

Chandrasekaran and Mukherjee [3] observed additional $0\,\frac{1}{2}\,\frac{1}{2}$ superlattice reflections in selected-area diffraction patterns obtained from martensite. They suggested that the martensite may be considered as a stacking modulated structure derived from the $\{1\,1\,0\}$ planes in NiAl. This structure would be similar to the martensite in Au–Cd alloys, analysed by Toth and Sato [4]. Chandrasekaran and Mukherjee [3] predicted the intensity of the electron diffraction reflections for the stacking modulated structure, but the calculated diffraction patterns did not reproduce the experimental data accurately.

The present work attempts to resolve the controversy regarding the crystal structure of the martensitic form of NiAl.

2. Experimental procedures

A ternary alloy Ni–30.3 at.% Al–6.6 at.% Cr was studied. Chromium was added since it is known to increase the oxidation resistance of NiAl [5, 6] and the author wished subsequently to make a detailed examination of the mechanical properties of NiAl alloy, having increased oxidation resistance [7]. Chromium can substitute for both Ni and Al in NiAl [8], the partition is, however, uncertain. Chromium is also known to affect the lattice parameter of NiAl [8]. Chromium

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*Present address: Central Electricity Generating Board, Gravesend Laboratories, Gravesend, Kent, UK.

additions to NiAl were, however, found to have no effect upon the nature of the phase transformations [9].

The material was prepared by argon arc melting, encapsulation in mild steel and extrusion at 1100° C. Discs were cut from the extruded material by spark machining and solution treated at 1300° C in pure argon or in a vacuum of 10^{-5} Torr. Specimens were water quenched from the solution treatment temperature. Thin foils were prepared by electropolishing in a Fischione "Twin Jet Electropolisher", in a solution of 5% perchloric acid in ethanol, at 50 V and −30° C. Specimens were examined at 200 kV in a JEM 200 electron microscope.

3. Results

On some occasions it was noticed that martensite did not form although the heat-treatment was not altered and this simulated the untransformed condition. Thus the crystal structure of the martensite could be compared with the untransformed condition, in which the crystal structure is ordered B2.

Fig. 1 shows the selected-area diffraction pattern obtained from this structure, for the ⟨1 0 0⟩ matrix beam direction. There are streaks parallel to the ⟨1 1 0⟩ directions. Russell and Edington [10] showed that these streaks indicate the presence of fine planar precipitates on the {1 1 0} matrix planes.

The crystal structure of the martensite was identified as body centred tetragonal, with lattice parameters $c = 3.2$ Å, $a = 2.56$ Å, and $c/a = 1.25$. In addition, a body centred orthorombic form of the martensite was found with $a_2/a_1 = 1.1$ ($a_1 \equiv a$ in bctet) and $c/a_1 = 1.25$. When specimens were annealed at 595° for 30 min, only a body centred tetragonal martensite was observed. Therefore, a possible explanation for the existence of a body centred orthorombic structure is that this structure forms in order to accommodate the stresses between individual martensite laths. The martensite plates are internally twinned. Enami *et al.* [2] determined the twinning elements* of the martensite as $K_1 = (1\,0\,1)_T$, $K_2 = (1\,0\,\bar{1})_T$, $\eta_1 = [1\,0\,\bar{1}]_T$ and $\eta_2 = [1\,0\,1]_T$. Present results are consistent with these conclusions.

Additional $0\frac{1}{2}\frac{1}{2}$ superlattice reflections in diffraction patterns sometimes arise from further ordering of NiAl during quenching. An example is shown in Fig. 2 for ⟨1 1 1⟩ beam orientation with the additional reflections arrowed. Fig. 3 shows the bright-field electron micrograph and the corresponding dark-field from the $0\frac{1}{2}\frac{1}{2}$ superlattice reflection. In the dark-field electron micrograph, the regions which contribute most to the $0\frac{1}{2}\frac{1}{2}$ reflection, appear as small white narrow regions.

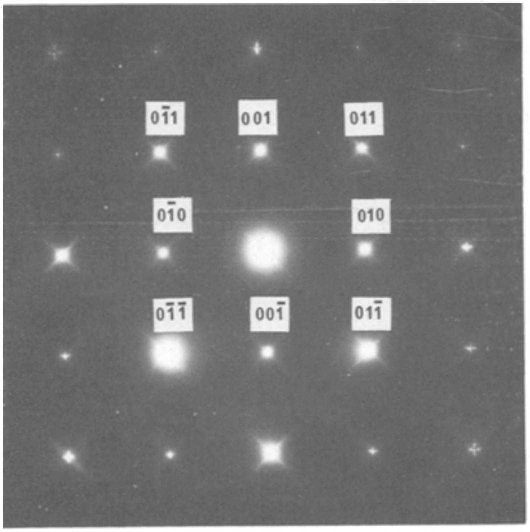

Figure 1 Selected-area diffraction pattern for the ⟨1 0 0⟩ beam direction, taken from a quenched untransformed specimen.

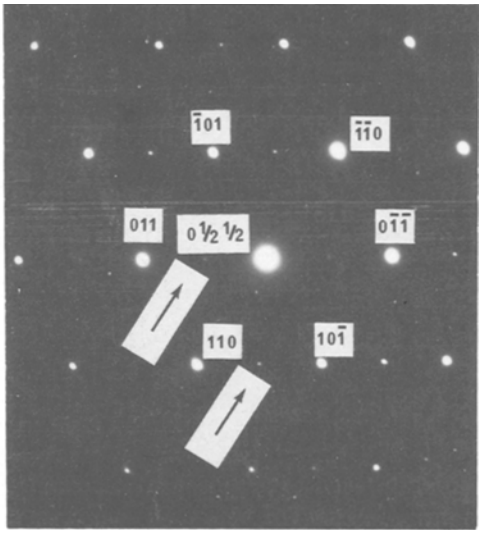

Figure 2 Selected-area diffraction pattern for a $[1\,\bar{1}\,1]$ matrix zone axis showing the $0\frac{1}{2}\frac{1}{2}$ superlattice reflections (arrowed).

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[*] The twinning elements $K_1 (1\,1\,1)_T$; $K_2 = (1\,1\,\bar{1})_T$; $\eta_1 = [1\,1\,\bar{2}]$ and $\eta_2 = [1\,1\,2]_T$ reported by Enami *et al.* [2] for the LI_0 crystal structure can be transformed into the bctet co-ordinates using the transformation matrices in the appendix.

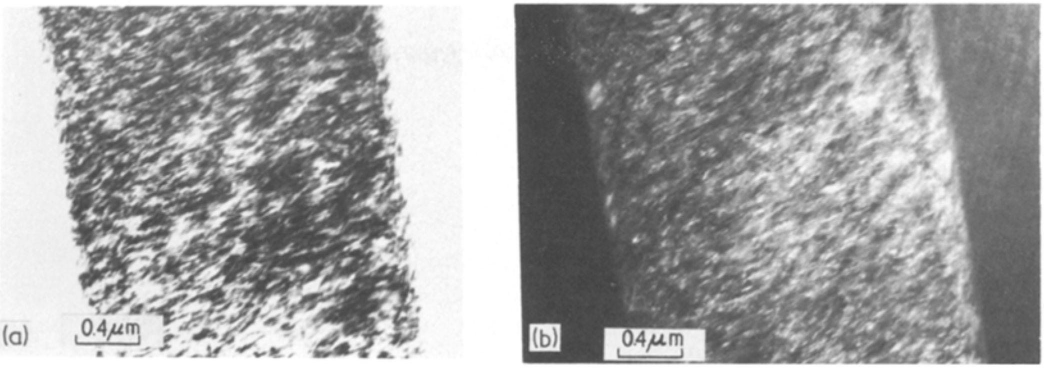

Figure 3 Bright-field (a) and dark-field (b) images of a martensite plate viewed along [1 $\bar{1}$ 1] zone axis. Dark field is formed using an "0 $\frac{1}{2}$ $\frac{1}{2}$" reflection.

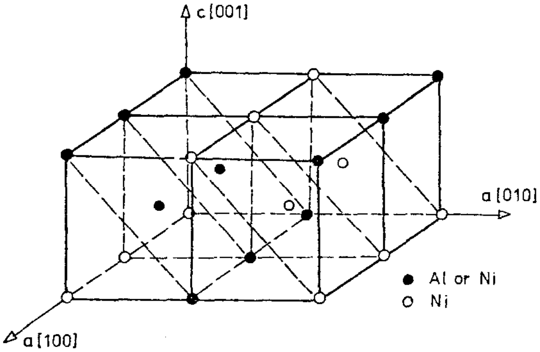

Figure 4 The crystal structure of the "superordered" martensite. Four unit cells are shown.

The crystal structure proposed to account for the presence of 0 $\frac{1}{2}$ $\frac{1}{2}$ superlattice reflections is shown in Fig. 4. This structure which is characterized by alternate stacking of Ni atoms and Ni or Al atoms on (0 1 1) planes, will be entitled "super-ordered". A possible mechanism which can produce the alternate stacking of Ni and Ni or Al atoms is a co-ordinated shear distance $\frac{1}{2}a\langle 1\ 1\ 1\rangle$ on every second (0 1 1) plane.

4. Discussion

It has been conclusively shown in this investigation that the hypothetical high temperature NiAl ordered structure, postulated by Rosen and Goebl [1], does not exist because untransformed quenched NiAl has a B2 crystal structure. The reflections reported by Rosen and Goebl [1] can be accounted for on the basis of the present proposed structure of the martensite and the Ni_3Al precipitates. The Ni_3Al precipitates were present in the samples of Rosen and Goebl [1] as a result of annealing their samples at 600° C [6]. In the table column (a) shows the reflections reported by Rosen and Goebl [1]; column (b) shows reflections that would arise from the presence of martensite as indicated by Fig. 4; and column (c) shows reflections which would arise from Ni_3Al precipitates. From the data of Rosen and Goebl [1], the lattice parameters of bc tet martensite and fc tet precipitates are determined as $c = 3.28$ Å, $a = 2.68$ Å and $c = 3.28$ Å, $a = 3.79$ Å, respectively. The values of c/a reported by Rosen and Goebl [1], and found in the present investi-

TABLE I Intensities of X-ray reflections reported by Rosen and Goebl [1] for the Ni–34 at. % Al alloy

Interplanar spacing d (Å)	Observed intensities I/I_0	hkl plane indices*		
		a	b	c
3.79	4	1 0 0		1 0 0; 0 1 0
3.28	5	0 0 1	0 0 1	0 0 1
2.68	5	1 1 0	1 0 0; 0 1 0	1 1 0
2.48	1	1 0 1		1 0 1; 0 1 1
2.07	100	1 1 1	1 0 1; 0 1 1	1 1 1
1.89	40	2 0 0	1 1 0	0 2 0; 2 0 0
1.64	20	2 0 1; 0 0 2	0 0 2	0 0 2
1.34	15	2 2 0	2 0 0; 0 2 0	0 0 2

* (a) Martensite structure proposed by Rosen and Goebl [1].
(b) Present martensite structure.
(c) Ni_3Al precipitate structure.

gation, are 1.22 and 1.25 respectively. The difference can be explained by the presence of Cr in the latter sample. A similar result has been obtained by Arkhangel'skaya *et al.* [7] on addition of Co or Fe to binary Ni–Al alloy samples.

The present results are consistent with the conclusions of Enami *et al.* [2] that the NiAl martensite can form from the high temperature NiAl B2 crystal structure by a process involving an inverse Bain correspondence. Enami *et al.*, however, did not observe that further ordering of NiAl occurs during quenching.

The data of Chandrasekaran and Mukherjee [3] can be explained satisfactorily by the structural model of the martensite proposed here. Dark-field images would, however, be required for conclusive interpretation of these results.

The crystal structure of the martensite in Fig. 4 (b c tet with $c/a = 1.25$) is intermediate between the NiAl (b c c) and Ni_3Al (f c c which is equivalent to b c tet with $c/a = 1.41$) equilibrium structures. Further ordering of the martensite occurs, probably because it is thermodynamically the most favourable form of the metastable NiAl. When an Ni_3Al crystal cell is considered as being inside four "super-ordered" NiAl crystal cells then the stacking of $\{1\,1\,0\}$ NiAl planes is characterized by alternate stacking of Ni atoms in one plane and both Ni and Al atoms in adjacent planes. In Ni_3Al, atoms are ordered in planes containing both Ni and Al atoms, whilst in the "super-ordered" martensite Ni and Al atoms are randomly distributed in such planes. Thus the formation of small clusters of Ni_3Al precipitates, in NiAl requires local ordering reactions. This mechanism for the formation of Ni_3Al clusters would result in the

$$(1\,0\,0)_{Ni_3Al} \parallel (0\,1\,1)_{NiAl}$$

$$[0\,0\,1]_{Ni_3Al} \parallel [1\,0\,0]_{NiAl}$$

orientation relationship between the "super-ordered" martensitic form of NiAl and the Ni_3Al precipitates. Such orientation relationship is inconsistent with the results of Moskovic [6] obtained from studies of aged martensite, in which the orientation relationship between the Ni_3Al precipitates and the martensite matrix is given by the transformation matrix

$$\begin{pmatrix} h_1 \\ k_1 \\ l_1 \end{pmatrix}_{Ni_3Al} = \begin{pmatrix} 1\,1\,0 \\ \bar{1}\,1\,0 \\ 0\,0\,1 \end{pmatrix} \begin{pmatrix} h_2 \\ k_2 \\ l_2 \end{pmatrix}_{NiAl}$$

for planes and

$$\begin{bmatrix} u_1 \\ v_1 \\ w_1 \end{bmatrix}_{Ni_3Al} = \begin{bmatrix} 1\,1\,0 \\ \bar{1}\,1\,0 \\ 0\,0\,2 \end{bmatrix} \begin{bmatrix} u_2 \\ v_2 \\ w_2 \end{bmatrix}_{NiAl}$$

for directions.

The proposed mechanism, however, may explain the rapidity of the formation of plate like precipitates on $\{1\,1\,0\}$ matrix planes, during quenching from the solution treatment temperature. The presence of excess Ni (above 50 at.%), in the ordered NiAl structure, is likely to be a contributory factor in the rapid decomposition of NiAl during quenching. It can be shown that in the Ni–30.3 at.% Al–6.6 at.% Cr alloy a minimum of approximately 26 out of 50 NiAl unit cells will have the Ni_3Al stoichiometry (assuming that all Cr atoms substitute for Al). This high proportion of unit cells, having the stoichiometry of Ni_3Al, implies that thermal fluctuations at the homogenization temperature may create large clusters of b c c Ni_3Al. These clusters, unstable at the homogenization temperature, will be frozen in, by rapid quenching.

5. Conclusions

(1) NiAl martensite has a body centered tetragonal structure with lattice parameters $a = 2.56$ Å, $c = 3.2$ Å and $c/a = 1.25$.

(2) The martensite plates are internally twinned. The twinning elements are $K_1 = (1\,0\,1)_T$, $K_2 = (1\,0\,\bar{1})_T$, $\eta_1 = [1\,0\,\bar{1}]_T$ and $\eta_2 = [1\,0\,1]_T$.

(3) Further ordering of NiAl during quenching, by a co-ordinated lattice shear, produces a "super-ordered" NiAl which is characterized by alternate stacking of Ni and Ni or Al atoms on (0 1 1) planes.

(4) Fine planar precipitates on $\{1\,1\,0\}$ form during quenching of Ni-rich NiAl.

Appendix

$(h_1k_1l_1)$ indices of a set of lattice planes in the LI_0 crystal structure are related to a set of parallel planes $(h_2k_2l_2)$ in the b c tet crystal structure by the transformation matrix

$$\begin{pmatrix} h_1 \\ k_1 \\ l_1 \end{pmatrix}_{LI_0} = \begin{pmatrix} 1\,1\,0 \\ 1\,1\,0 \\ 0\,0\,1 \end{pmatrix} \begin{pmatrix} h_2 \\ k_2 \\ l_2 \end{pmatrix}_{b\,c\,tet}$$

a set of parallel directions $u_1 v_1 w_1$ in the LI_0 crystal structure are related to a set of parallel directions $u_2 v_2 w_2$ in the b c tet crystal structure by the transformation matrix

$$\begin{bmatrix} u_1 \\ v_1 \\ w_1 \end{bmatrix}_{LI_0} = \begin{bmatrix} 1\,1\,0 \\ 1\,1\,0 \\ 0\,0\,2 \end{bmatrix} \begin{bmatrix} h_2 \\ k_2 \\ l_2 \end{bmatrix}_{\text{b c tet}}$$

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